Printing Meets Lithography

FEATURE

by Bruno Michel

Soft approaches may challenge optical lithographies

Six years ago, our team at IBM set out to find an alternative to optical lithography by developing a novel type of lithography that provides high resolution based on classical flexography printing—the transfer of a pattern from an elastomeric stamp to a solid substrate by conformal, or intimate, contact. Our main effort sought to enhance the accuracy of this printing process to a precision comparable to that of optical lithography to create a low-cost, large-area, high-resolution patterning process. After having developed and tested several printing-based alternative-patterning approaches, we also found that stamps are useful in a new form of optical-contact lithography.

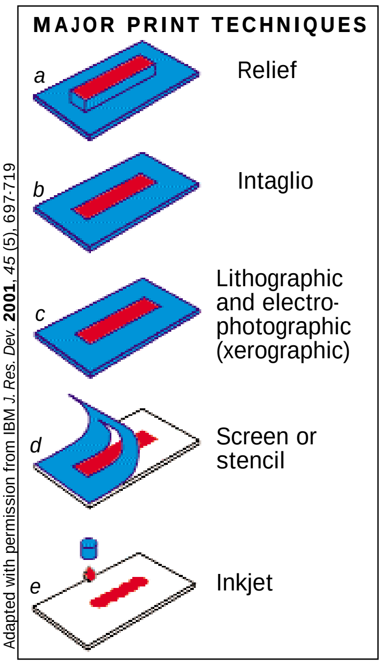

Figure 1. Red areas depict how ink is accepted on the stamp (blue in a–c) and applied to the substrate (white in d and e). Transfer of ink from the stamp to the target substrate via a rubber plate (offset printing) is possible with most of these five techniques.

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Printing

Printing ranks among the most significant technological developments in human history, for it created the capability to distribute ideas and ensure their survival over generations. It was originally developed for the exchange and storage of information adapted to human vision, which requires pattern and overlay accuracy down to 20 µm for high-quality reproduction.

All printing processes logically divide into two steps. The first defines an accurate pattern, and the second brings it close enough to the substrate to execute the desired process—ink transfer, chemical reaction, sealing, or optical exposure.

Five major printing processes exist today that entail the contact transfer of a pattern (Figure 1):

- Relief printing—a process that transfers an image from a raised surface—includes letterpress and flexography.
- Intaglio printing or gravure is the inverse of relief printing, where an image is transferred from a sunken surface.
- Lithography uses a chemically patterned flat surface with areas that accept ink and areas that repel ink.
- Screen or stencil printing transfers an image by passing ink through openings in a stencil applied to a screen substrate.
- Electrophotography creates an image by selectively discharging areas of a photoconductor drum to directly transfer a toner powder.

In addition, ink-jet printing, which does not entail the contact of a stamp with a substrate, has become important for pattern generation and replication.

In a few cases, traditional printing processes have been used for technological patterning—printed circuit boards and integrated-circuit packaging in the electronics industry, for example. However, tooling and process limitations generally have precluded printing structures smaller than 20 µm in the industry. Thus, most of the high-resolution patterning performed today is done with step-and-repeat projection lithography.

Printing approaches regained attention in 1993, when Amit Kumar and George M. Whitesides discovered that a polymer inked with an alkanethiol (a fatty-acid-like molecule with the acid changed to a reduced sulfur group) and brought into contact with a gold-coated surface can form a monolayer of the thiol molecules in the areas of contact. This process, called microcontact printing, is revolutionary because it transfers only a molecular monolayer of ink to a surface.

Conformal contact in high-resolution printing requires macroscopic adaptation to the overall shape of the substrate and microscopic adaptation of a soft polymer layer to a rough surface for intimate contact without voids. The stamps we use consist of a patterned elastomeric layer attached to a backplane of thin, bendable metal, glass, or polymer. In this hybrid stamp, the elastomer compensates for local surface roughness amplitudes of up to 1 µm, whereas the flexibility of the backplane (Figure 3) compensates for the bending of the substrate.

Soft lithography

Soft lithography is a general term for several alternative techniques to photolithography for fabricating micro- and nanostructures. They rely on the replication of a patterned elastomeric stamp made from a master that can be inked with a monolayer-forming ink. The stamp is then used to print a pattern that selectively protects a noble-metal substrate during a subsequent etch (Figure 2).

Examples of devices made using soft lithography are scarce and include relatively large structures. Among them are arrays of metal oxide on semiconductor field-effect transistors with a gate size of 20 µm, arrays of aluminum–silicon Schottky diodes with 2- to 100-µm gaps, and electrodes for organic electronic applications. Compelling reasons to switch to this new technique are the ability to process small structures and to pattern materials that are incompatible with resist processes.

The key elements of soft-lithography technologies are the master, elastomer, stamp, resist-forming ink, inking methods, and printing tool.

Both printing and soft lithography rely on onefold magnification (1×) masks, which makes fabricating a mask or master more challenging than making the 4× to 5× masks used in projection lithography. The master we use is a structured silicon or resist surface with a vertical inverse of the desired pattern. Stamps are created by pouring liquid poly(dimethylsiloxane), or PDMS, prepolymers on the master and curing them at temperatures between 20 and 80 °C for up to 48 hours. The polymeric surface of the stamp is well suited for microcontact printing of alkanethiols on gold, but other types of inks may require a chemical treatment of the stamp surface.

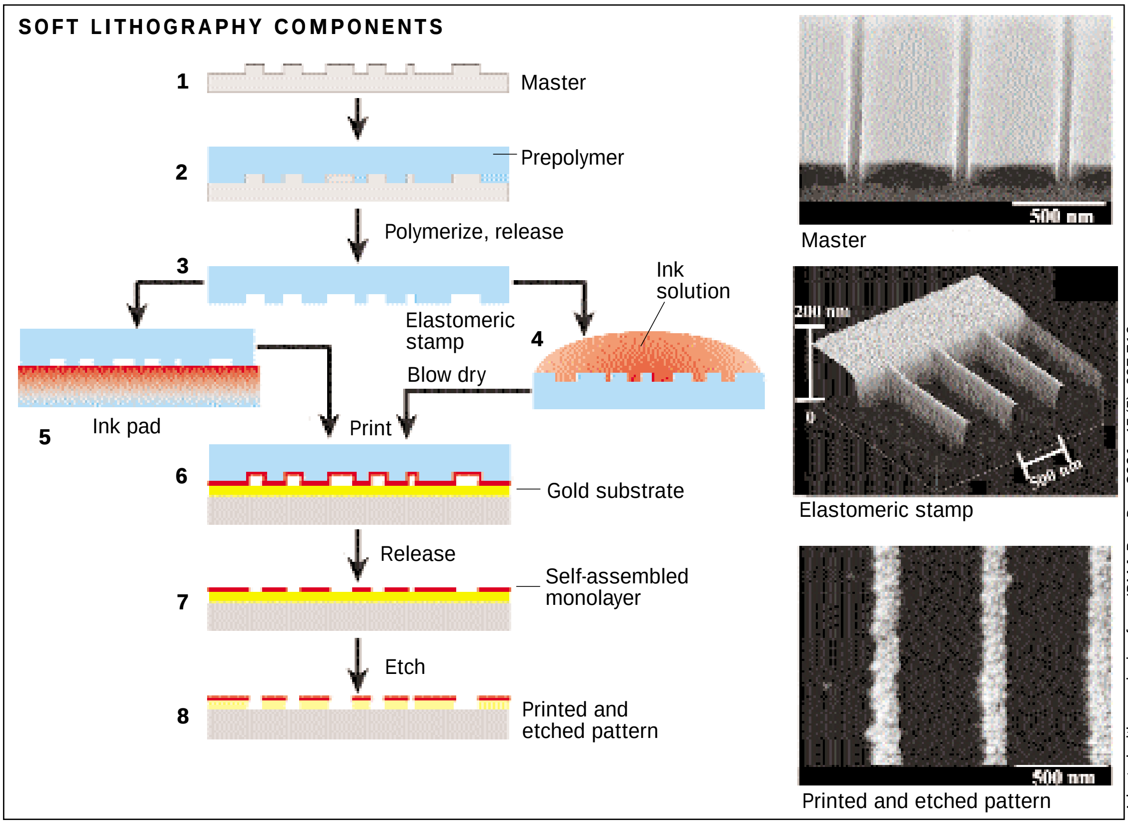

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Figure 2. A prepolymer (2) covering the master (1) is cured by heat or light and demolded to form an elastomeric stamp (3), which is inked by immersion (4) or with an ink pad (5) and printed onto the substrate (6), forming a self-assembled monolayer, which is transferred into the substrate by a selective etch. Scanning electron micrographs show the master, image of the stamp, and the printed and etched pattern.

Alkanethiols self-assemble on noble-metal surfaces such as gold, silver, and copper to form dense, ordered monolayers. These monolayers allow control of wettability, adhesion, chemical reactivity, electrical conduction, and mass transport to the underlying metal. To print thiols on metal surfaces, we first ink the stamp by touching it with a soft surface that has been soaked with ink. A short contact of the stamp with the metal transfers the thiol molecules and forms a patterned monolayer that acts as a selective mask in a wet-etch process. Microcontact printing can reproduce high-resolution patterns in gold, silver, or copper that can be used to carry electrical currents or act as secondary etch masks for certain chemical processes and for shallow reactive ion etches. In recent experiments, we have reproduced 100-nm-wide lines and dots. Applications using nondiffusive inks (macromolecules) or the confinement of light can achieve higher printing accuracy. Patterning semiconductors requires the use of a sacrificial-gold mask on a standard resist. Otherwise, the incompatibility of gold with semiconductor processes will allow only specialized niche applications for microcontact printing of alkanethiols, such as patterning of diffractive optical elements.

Stamp fabrication

One of our primary goals was to improve the minimum achievable feature size, or critical dimension (CD). In the past, the CD of soft lithography was limited by the choice of commercial siloxane as the stamp material, which proved to be too soft to define features smaller than 500 nm. We formulated harder stamp materials with sufficient toughness for large-area, high-resolution printing applications that produced feature sizes as small as 80 nm. Currently, the smallest size moldable with a high aspect ratio is 50 nm.

The most challenging stamp designs are those with a broad dynamic range of pattern sizes, that is, the ratio of the smallest printed feature to the largest unprinted area. This is because the smallest feature determines the typical depth of patterns, which imposes a low aspect ratio on large recessed zones, which are thus prone to collapse.

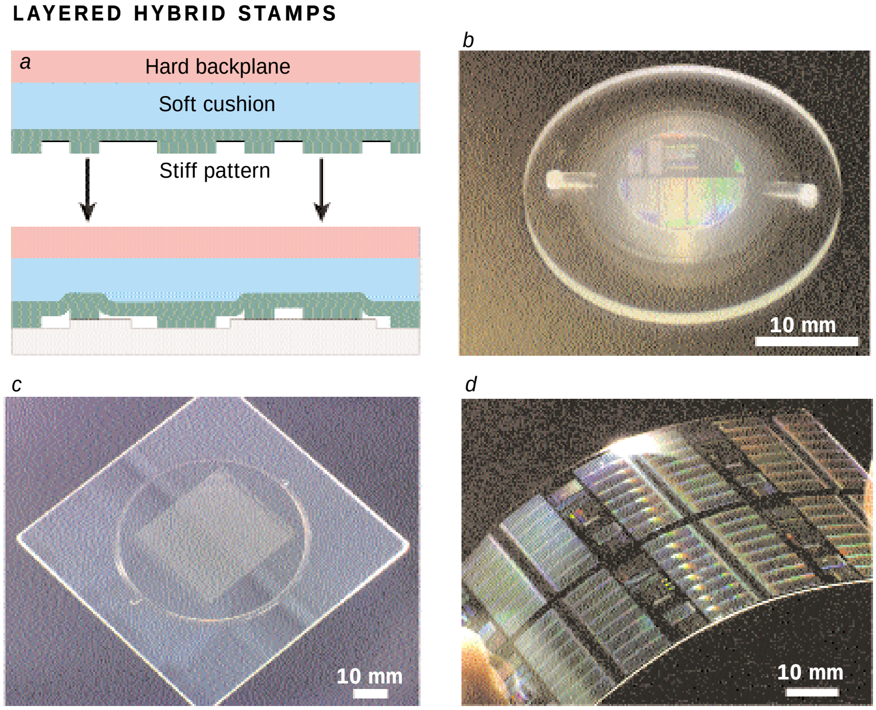

Figure 3. Trilayer stamp shows improved adaptation to an uneven substrate (a). Trilayer stamp with 270-nm features (b). Bilayer stamp with 5-µm features on a 125-mm glass plate (c). Two-layer thin-film stamp composed of a 100-µm glass backplane and a 30-µm polymer film with 270-nm features.

Complex masters created in more than one lithography step can be used to create stamps that can handle broader dynamic ranges of patterns but are more expensive.

The main function of a printing tool is to establish the contact and facilitate the release of a stamp from a substrate with precise control over the printing time, the mechanical forces, and the placement of the stamp on the substrate. For our tool we used an approach in which a thin-film stamp (Figure 3) is wrapped around a cylinder and rolled over the substrate, as in a rotary press.

This approach uses a thin-film stamp and a 400-mm-radius printing cylinder. For printing areas on the order of 100 × 100 mm, we did not build a full cylinder but only an arc similar to the rockers of a rocking chair, which is mounted on a modified mask aligner. With this tool, defect counts are already low enough for printing reliable structures such as high-resolution diffractive optical elements and low-resolution microelectromechanical-system patterns in large numbers.

Applications

Arrays of surface-bound biomolecules find applications in biosensors, chromatography, and other analytical procedures. Among these applications, diagnostic immunoassays and DNA sensing are driving the effort to miniaturize biological assays and to conduct many assays at once. Our technique significantly improves the extraction of molecules from fluids and places them in arbitrary patterns on surfaces, which is important to research and analysis in biotechnology.

The main advantage of printing over pipetting, inkjet spotting, and pin spotting for making arrays is its capability to process large bioactive surfaces in one run. To expand the range of possible applications, we devised schemes for parallel patterning of the same surface with different proteins.

Transferring chemical reagents from an elastomeric stamp to a substrate can be used to direct the electroless deposition (ELD) of copper. This process entails the reduction of a salt from solution onto a surface using a reducing agent as the source of electrons. The presence of a catalyst on the surface is necessary to initiate ELD before the deposition can proceed in an autocatalytic manner. All previous approaches used solvents that interfere with the chemical and topological integrity of PDMS stamps. For this reason, we examined the printing of palladium(II)-based catalytic precursors soluble in solvents that are compatible with high-resolution PDMS stamps. For our application, the evaporation of a thin layer of titanium onto a substrate, such as a silicon wafer, proved the best preconditioning method.

This approach led to copper structures with linewidths of 170 nm, for example, when high-resolution stamps provided the pattern. Copper grains appear to be continuously connected and form the lines with good accuracy. We believe that feature sizes of about 50 nm are achievable by combining improved stamp fabrication with an optimized copper ELD process.

PDMS is transparent for wavelengths down to ~250 nm, and when it makes conformal contact with a substrate, the reflection of light at the interface is minimized. Thus, structured PDMS stamps selectively guide electromagnetic fields through the interfaces in contact. These so-called light-coupling masks (LCMs), or light stamps, consist of a transparent backplane and a PDMS material with a refractive index matching the resist, and in some cases an absorbing layer in recessed zones. They are placed on a resist-covered surface and exposed to short-wavelength light. As in other areas of soft lithography, the mask must have the same feature sizes as the final product. The small protruding features on the stamp, which are surrounded by air gaps, collimate and intensify the incoming light, thus exposing the photoresist in a patterned fashion.

Simulations and experiments reveal that the LCM technique is wavelength-dependent but can approach the physical limit of resolution more closely than can hard-contact lithography. Experiments have shown that features as small as 120 nm at a pitch of 240 nm can be reliably reproduced. The light stamp demonstrates that there is no strict boundary between printing and optical or X-ray contact lithography—it seems that both approaches can yield comparable results.

Outlook

Soft lithography makes use of almost all replication schemes known from classical printing and introduces a few novel schemes. We have shown that high accuracy is achievable with soft lithography, but alignment issues remain a challenge. Adaptive approaches could greatly relax the demands for long-range accuracy for a slightly elastic system that is capable of physically determining the misalignment by mechanical contact and adapting itself accordingly. However, the technical feasibility of such concepts has yet to be demonstrated.

In the semiconductor industry, optical lithography approaches have been pursued with much more vigor than have printing approaches. Therefore, it is no surprise that they predominate in the crucial patterning steps. The development of soft lithography initially proceeded rapidly and separately from the printing industry. Now, however, it will presumably merge with printing to create a new technology that may challenge optical lithographies in terms of throughput, cost per area, and high-resolution pattern replication.

Further reading

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BIOGRAPHY

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